



# On some explosive alloys of zinc and the platinum metals

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ON SOME EXPLOSIVE ALLOYS OF ZINC AND THE PLATINUM METALS. BY H. SAINTE-CLAIRE DEVILLE AND H. DEBRAY.

SOME time before the sickness of my dear and illustrious master Henri Sainte-Claire Deville, we had undertaken to return to some points in order to complete our old researches respecting platinum. Our work, as regards the division of the osmides, was almost finished, when it was interrupted by his sickness and death. I have had to terminate it; and today I present the result to the Academy.

It is known that the osmides cannot be divided by mechanical action. If for example, one essays to pound them in a tempered steel mortar, the osmide of iridium penetrates into the material without being either blunted or broken.

If, however, it be fused with 25 or 30 times its weight of zinc, and if after the mixture has been kept for some hours at an incipient red heat it then be more heated in order to volatilize all the zinc, there remains a spongy mass, easily divided, and, in this state, completely and with facility attacked by the mixture of nitrate and binoxide of barium which we have employed for oxidizing the two metals of the osmide and to render them soluble in acids. As it is easy to eliminate baryta from its solutions, the analysis of the osmide then becomes possible.

What is the part played by zinc in this division? by what mechanism is it effected? are questions which we had not then examined, contenting ourselves for the moment with a practical result sought in vain by Berzelius, which facilitated our entering upon that study of the platinum metals which has occupied us for many years.

I. Some osmide of iridium is thrown into some zinc heated to dull redness and which has been previously well cleaned with sal-ammoniac. A brisk disengagement of heat is produced. The mass is kept melted at this temperature during five or six hours, in order to attack completely the large grains of osmide. The cold button is then dissolved in dilute hydrochloric acid. The solution of the zinc takes place with great violence; and there remains a blackish residue having the appearance of graphite, which contains all the noble metals of the osmide. The greater part of the iron existing in this material is dissolved at the same time as the zinc; on the other hand, there remains a notable proportion of zinc combined with the metals of the osmide, and it is not removed by prolonged contact with concentrated hydrochloric acid.

This residue, well washed, and dried at 100°, diffuses in the air a slight odour of osmic acid. Heated to nearly 300° it suddenly ignites, almost with explosion, spreading fumes of zinc and abundant vapour of osmic acid. As this deflagration took place *in vacuo*, without any sensible liberation of gas, and of course without the

production of oxide of zinc and osmic acid, we must conclude that at about  $300^{\circ}$  the substance undergoes a change of state accompanied by a large disengagement of heat. In air the change of state is immediately followed by combustion, which augments the evolution of heat.

The residue is only partially attacked by concentrated nitric acid or aqua regia. It is quickly and completely oxidized when thrown into a mixture of fused potass and potassium nitrate; it must even be thrown in in small portions, the mixture being but little heated, to avoid too strong a deflagration when the divided material touches the surface of the oxidizing liquid. If one wishes to make use of this residue either for the analysis of the osmide or to extract the metals which it contains, it is better to mix it with anhydrous baryta and barium nitrate: one can then heat it without fear of losing the substance, which is then attacked totally and easily.

This substance is evidently a complex mixture of various alloys which zinc is capable of forming with the platinum metals; we were therefore induced to examine more closely those different combinations.

II. Osmium simply dissolves in zinc. When the fused button of this metal with osmium in a state of division is acted upon by hydrochloric acid, there remains pure osmium with a crystalline appearance.

Palladium and platinum, treated in the same manner, leave a residue consisting of alloys which undergo no isomeric modification when heated *in vacuo*. Rhodium, on the contrary, and iridium and ruthenium especially, as one of us has already proved\*, combine with zinc with much liberation of heat; and when the zinc button is dissolved in hydrochloric acid, residues are obtained which are susceptible of undergoing a true isomeric modification accompanied by a brisk liberation of heat, without loss of gas, when heated in a vacuum above  $300^{\circ}$ . Before the liberation of heat, the blackish residues would be more or less readily attacked by aqua regia. They lose this property after the liberation of heat, and then take the metallic appearance.

The thermal phenomenon which accompanies the change of state of the iridium residue is so marked that it may serve for the recognition of the presence of small quantities of iridium in platinum (1 or 2 per cent. for example). The metal to be assayed is dissolved in a large excess of zinc; and the button is acted upon by dilute hydrochloric acid; the residue, well dried, raised to a temperature above  $300^{\circ}$  in a platinum capsule becomes incandescent at various points. Ruthenium and rhodium produce similar effects.

III. In brief, osmium is the only platinum metal which does not retain zinc when its alloy with a large excess of zinc is treated with an acid capable of dissolving that metal. The other metals obstinately retain a notable proportion of it (on the average 10 to

\* *Comptes Rendus*, t. xc. p. 1150.

12 per cent.); and the metals which are insoluble in aqua regia (rhodium, iridium, and ruthenium) then remain in the state of peculiar products, without metallic lustre, which seem to be an allotropic modification of the true alloys possessing a metallic appearance.

The action of zinc upon the osmide of iridium is thus accounted for naturally. If the heat liberated in the combination of iridium and zinc much exceeds the heat of combination of osmium and iridium, the osmide, in conformity with the laws of thermochemistry, will be destroyed by the zinc; the osmium dissolves and may crystallize in the excess of metal; the iridium and the other metals remain combined with the zinc. It is the residue from the action of the hydrochloric acid upon this alloy with excess of zinc that constitutes the explosive substance above considered. In fact the heat liberated in the union of zinc with iridium, ruthenium, and rhodium, which are the dominant metals of the osmide, is truly enormous: on adding, for instance, 1 part of iridium to 30 or 40 per cent. of melted zinc at a temperature below a red heat, there is combination accompanied by actual incandescence of the whole mass of metal; it is the same with the two other metals. If all the zinc be driven out by heat (as was done by us in our old experiments), the hardly fusible metals of the osmide, free or alloyed, remain in a state of extreme division, in which they are much more readily attacked than the natural osmide.

In an early Note we shall speak of facts observed in the solution of the platinum metals in copper.—*Comptes Rendus de l'Académie des Sciences*, June 12, 1882, t. xciv. pp. 1557-1560.

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ON THE REACTION-CURRENT OF THE ELECTRIC ARC. BY M. JAMIN,  
WITH THE ASSISTANCE OF M. G. MANEUVRIER.

The two currents, in alternately opposite directions, given by Gramme's self-exciting machine are absolutely equal; consequently they do not decompose water, and a tangent-compass intercalated in the circuit undergoes no deflection, since the contrary effects following at very close intervals destroy one another. This destruction of the effects is kept up when one or several burners are put into the circuit, provided that the two carbons are equal, disposed in exactly the same manner, and are heated equally.

If eight or ten Bunsen elements be introduced into the total circuit, they communicate to the compass a deflection  $\delta$  when the machine is at rest, and a deflection  $\delta'$ , absolutely equal to  $\delta$ , when the machine is working.

	$\delta$ .	$\delta'$ .
First experiment . . . . .	32	33
Second experiment . . . . .	38	38.45
Third experiment . . . . .	33	34.10

This equality proves that the resistance of the wires of the machine does not vary, whether the machine be at rest or in motion;